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Thermodynamics of redox processes and kinetics and mechanism of electron self-exchange reactions in the Bis(N,N-diethyldithiocarbamato)copper(II)/iodine/dichloromethane system

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Abstract

The thermodynamics of complex formation between Et4NI and I2 in CH2Cl2 and the redox processes in the bis(N,N-diethyldithiocarbamato)copper(II) [CuIIL2]/I2/CH2Cl2 system have been studied spectrophotometrically. The reversibility of the reactions of formation of copper(III) complexes was established and their thermodynamic parameters determined: CuIIL2 + 3/212← → [CuIIIL2]I3 {logK = 5.80 (298K), ΔH = -35.0 kJ·mol-1, and ΔS = -6.7 J·K-1·mo1-1} and [CuIIIL2]I3 + I2 ← → [CuIIIL2]I5 {logK = 2.02 (298 K), ΔH = -11.1 kJ·mol-1, and ΔS = 1.3 J·K-1·mol-1}. The rate constants and activation parameters for the electron self-exchange reactions between CuIIL2 and [CuIIIL2]In (n = 3, 5) in the CD2Cl2 solutions were determined by NMR line-broadening of the ligand L protons: ke = 3.0·108 M-1·s-1 (298 K), ΔH≠ = 6.1 kJ·mol-1, and ΔS≠= -62.3 J·K-1 mol-1. To account for the kinetic parameters, an unusual mechanism for the self-exchange reaction was suggested. This mechanism involves the prior formation of the CuIIL2InCuIIIL2 intermediate, in which considerable delocalization of electron density through the orbitals of copper and bridging iodine atoms is achieved, followed by electron transfer. The formation of the intermediate was supported by ESR data and quantitative analysis of the activation parameters with the use of quantum chemical computations by the DFT method at the B3LYP/3-21G* level.

Keywords

Copper, Electron-transfer kinetics, Reaction mechanisms, Redox reactions thermodynamics, S ligands